Base-Catalyzed Isotopic Exchange of Molecular Hydrogen. III.[1] Transition-State vs. Initial-State Solvation in the Dimethyl Sulfoxide–Water System

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Abstract: The kinetics of isotopic exchange between D_2 and H_2O under catalysis by OH^- have been determined in dimethyl sulfoxide–water mixtures as a function of temperature. Activation parameters have been derived. It is found that $\Delta H^\ddagger$ decreases by 7 kcal/mol over the range 0–50 mol % Me_2SO and then rises slightly. $\Delta S^\ddagger$ passes through a minimum near 60 mol % Me_2SO. As a result, $\Delta G^\ddagger$ decreases only moderately (3.5 kcal/mol) over the full range of medium composition. Transition-state enthalpies of transfer, $\delta\Delta H_{tr}{}^t$, from water to aqueous Me_2SO, have been evaluated using the enthalpies of activation and the known enthalpies of transfer of OH^- and D_2. The $\delta\Delta H_{tr}{}^t$ term is endothermic throughout the range of solvent composition; for 96.9 mol % Me_2SO, $\delta\Delta H_{tr}{}^t$ is 13.7 kcal/mol, compared with a value of 17.5 kcal/mol for hydroxide ion. This points to a transition-state structure with considerable charge localization on oxygen, resulting in transition-state desolvation in Me_2SO-rich media. This conclusion allows certain mechanisms for the D_2–OH^- exchange to be excluded. Currently favored are a mechanism in which an H_2O molecule participates in the rate-determining step, providing electrophilic assistance for removal of D^- during attack by HO^- on D_2, and one involving rate-determining replacement of an H_2O of solvation from hydroxide ion by D_2 followed by rapid isotopic exchange.

We had previously reported[1,3] on the rate of the hydroxide ion catalyzed isotopic exchange of molecular deuterium in dimethyl sulfoxide (Me_2SO)–water mixtures at 65°C (eq 1).

$$D_2 + H_2O \xrightarrow[Me_2SO]{OH^-} HD + HOD \tag{1}$$

It had been anticipated that the rate enhancement accruing from use of Me_2SO media would make this isotopic exchange[4] of value in heavy-water separation.[5] A number of H/D exchange reactions in which proton transfer from substrate to base is rate-determining exhibit rate enhancements of 10^{10} or more when the medium is changed from aqueous (or alcoholic) to ~99 mol % Me_2SO.[6-8] However, in our study the rate of exchange increased only by 10^4 on changing the medium from water to 99.6 mol % Me_2SO.[3] Expressed in terms of rate correlation with the H_- function,[9,10] a reaction exhibiting a rate enhancement of 10^{10} when the medium is changed from H_2O to 99.6 mol % Me_2SO would have a slope of 0.7 in the log k vs. H_- plot. In contrast, reaction 1 shows a much shallower dependence of log k on H_-; one obtains a slightly curved plot with an initial slope of 0.23 and final slope 0.36.[3]

A number of mechanisms were considered in order to account for this and other characteristics of the D_2 exchange process (vide infra). However, we felt that the data at hand, obtained at a single temperature, were insufficient to distinguish among at least four of the possibilities.[1]

Desolvation of the "hard" hydroxide ion, resulting from the inability of Me_2SO to form hydrogen bonds with anions, is believed to be the main factor responsible for the rate-enhancing properties of Me_2SO and other dipolar aprotic media, relative to protic solvents. Desolvation of the transition state has been thought to be less important in most cases and in fact evidence has been presented that in some reactions there is *increased* solvation of the transition state in dipolar aprotic media, particularly when charge could be delocalized and a polarizable transition state resulted.[11-13]

In recent years, quantitative data have become available on enthalpies of transfer, $\delta\Delta H_{tr}$, of neutral and ionic species, between hydroxylic and dipolar aprotic media.[12-18] Focusing on the reaction at hand, $\delta\Delta H_{tr}$ data are available for transfer from H_2O to Me_2SO–H_2O mixtures for ^-OH[16] as well as for H_2.[18] In Me_2SO rich media, the $\delta\Delta H_{tr}$ term for OH^- far exceeds that for H_2. The sum of the terms for H_2 and OH^- for transfer from H_2O to 99 mol % Me_2SO is ca. 20 kcal/mol. This represents a very large desolvation energy and, if it were all utilized kinetically, the resulting rate enhancement would be ca. 10^{14}. In contrast, as we have seen, the observed rate enhancement is only 10^4. Evidently the transition state must also be profoundly affected by the medium change. In order to learn more about the transition state behavior, we have undertaken a study of the activation parameters of the reaction, and the results are reported herein.

Experimental Section

Deuterium gas was stored as uranium deuteride or used directly as supplied by Matheson. Purification and storage of Me_2SO has been described elsewhere.[1,18] Deionized distilled water was used. The tetramethylammonium hydroxide was a standardized solution of 25% aqueous Me_4NOH (Matheson Coleman and Bell).

Exchange of D_2 was effected in a closed glass reaction vessel containing the basic solution and D_2 gas at 1 atm pressure, under conditions of thorough mixing, with the vessel submerged in a constant-temperature oil bath. Details of the design of the reaction vessel, the preparation and transfer of solutions, and the general procedure were given previously.[1]

Reaction was followed by sampling the vapor phase and analyzing for $D_2/HD/H_2$ by mass spectrometry. Exchange rates were obtained from plots of log (mole % D_2) vs. time, by means of least-squares calculation. The resulting first-order rate constants, which apply to the "vapor phase" rate of exchange of $D_2/HD/H_2$, were converted to in-solution rate constants by multiplying by the factor (total moles of D_2 in the system)/(moles of D_2 dissolved in the liquid phase). This factor was calculated from the solubility[19] of D_2, the total volume of the reaction vessel, and the solution volume. The correction factor varied from 95 to 180, becoming greater as the temperature was lowered. The resulting rate constants are believed to be accurate within ±5% over the solvent composition range 0–95 mol % Me_2SO. In >95% Me_2SO some decomposition of the base set in, so that only initial rates were measurable (1 half-life or less); the resulting uncertainty in the rate data at ~99% Me_2SO is 20%. In the Me_2SO rich media base-catalyzed equilibration of the hydrogen isotopes of CH_3SOCH_3 and H_2O molecules is facile,[20,21] so that the effective H:D ratio remains large under all conditions of exchange. The base concentration was constant for a given solvent system but was varied from one solvent to another so as to bring the reaction rate within a conveniently measurable range (Table I).

Table I. First-order, In-Solution Rate Constants (sec^{-1}) for D_2 Exchange in Me_2SO–Water–Me_4NOH

Me_2SO, mol %: Me_4NOH, M:	20.2 0.460	40.1 0.361	59.0 0.415	77.9 0.134	87.5 0.096	96.9 0.022
Temp, °C						
35.0			3.72×10^{-4}	2.44×10^{-4}	4.55×10^{-4}	5.05×10^{-4}
50.0	8.65×10^{-5}	3.28×10^{-4}	1.45×10^{-3}	8.41×10^{-4}	1.76×10^{-3} 1.60×10^{-3} 1.63×10^{-3} 1.73×10^{-3}	2.06×10^{-3}
65.0	3.78×10^{-4}	1.14×10^{-3}	4.20×10^{-3}	3.22×10^{-3}	5.75×10^{-3}	8.30×10^{-3} 9.08×10^{-3}
80.0	1.56×10^{-3}	3.75×10^{-3}	1.36×10^{-2}	9.25×10^{-3}	1.72×10^{-2}	2.32×10^{-2}

Table II. The Activation Parameters E_a, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ for D_2 Exchange in the Me_2SO–Water–Me_4NOH System

Me_2SO, mol %:	0	20.2	40.1	59.0	77.9	87.5	96.9
E_a, kcal/mol[a]	24.7 ± 1[d]	21.9 ± 0.8	18.4 ± 0.7	17.1 ± 0.5	17.6 ± 0.5	17.5 ± 0.5	18.8 ± 0.5
$\Delta S^\ddagger$, cal/(deg mol)[b]	-7.2 ± 3[d]	-10.6 ± 2.5	-19.0 ± 2.5	-20.7 ± 2.0	-16.9 ± 2.0	-15.5 ± 2.0	-7.6 ± 2.0
$\Delta G^\ddagger$, kcal/mol[c]	26.5[d]	24.8	24.1	23.4	22.6	22.0	20.7

[a] Calculated from experimental data at base concentrations indicated in Table 1. [b] Calculated from derived rate constant data at 0.011 *M* Me_4NOH at 65°. [c] $\Delta G^\ddagger$ calculated at 65°C from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$; $\Delta H^\ddagger = E_a - RT$. [d] Data derived from work of W. K. Wilmarth et al., *J. Amer. Chem. Soc.*, 75, 4549 (1953) and U. Schindewolf, *J. Chim. Phys.*, 60, 124 (1963).

Results

The first-order in-solution rate constants for base-catalyzed D_2 exchange measured at several temperatures from 35 to 80°C over the range of solvent composition are presented in Table I. From these data energies of activation, E_a, were calculated from plots of log k vs. $1/T$. The individual data points fell within 5% of the least-squares lines for these plots. Entropies of activation, $\Delta S^\ddagger$, were obtained using the equation recommended by Bunnett,[22] with rate constants for 0.011 M base at 65°C obtained by extrapolation or interpolation of the k_{obsd} vs. [Me_4NOH] data in Table II of ref 1. Free energies of activation, $\Delta G^\ddagger$, at 65°C were obtained from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, although direct calculation from $k_2 = (kT/h)\exp(-\Delta G^\ddagger/RT)$ gave comparable data. The resulting values of $\Delta G^\ddagger$, $\Delta S^\ddagger$, and E_a for the various Me_2SO-water mixtures are given in Table II. A graphical representation of $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ (kcal/mol) as a function of medium composition is shown in Figure 1.

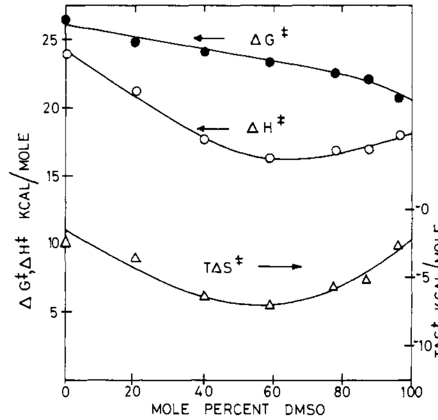


Figure 1. Activation parameters for OH^- catalyzed exchange of D_2 as a function of medium composition in the H_2O-Me_2SO system.

Discussion

Compensation of Enthalpies and Entropies of Activation. It is seen (Table II and Figure 1) that $\Delta H^\ddagger$ decreases substantially as the Me_2SO content is increased from 0 to 50 mol %, but it effectively levels out beyond this composition. The $\Delta S^\ddagger$ term also decreases from 0 to 50 mol % Me_2SO, passing through a minimum in the region of 60 mol % Me_2SO, and thereafter rises sharply. Thus there is an effective compensation[22-25] between $\Delta H^\ddagger$ and $T\Delta S^\ddagger$, with the result that $\Delta G^\ddagger$ is a slightly decreasing function over the entire range of solvent composition.

Enthalpies of Transfer. Transition-state enthalpies of transfer, $\delta\Delta H_{tr}{}^{t}$, from water to aqueous Me_2SO, can be evaluated by combining the activation parameters (Table II) with literature data on the enthalpies of transfer of deuterium gas, $\delta\Delta H_{tr}{}^{D_2}$, and of hydroxide ion, $\delta\Delta H_{tr}{}^{OH^-}$. The term $\delta\Delta H_{tr}{}^{D_2}$ is available from measurements of heats of solution of hydrogen and/or deuterium in H_2O-Me_2SO mixtures.[18,19] Enthalpies of transfer of single ions are not measurable directly but can be derived from measurements on salts by using certain extrathermodynamic assumptions,[11,17] namely that $\delta\Delta H_{tr}(Ph_4As^+) = \delta\Delta H_{tr}(Ph_4B^-)$. This has yielded $\delta\Delta H_{tr}{}^{OH^-}$ data for the entire H_2O-Me_2SO range of solvent compositions.[15] Interpolated $\delta\Delta H_{tr}$ values pertaining to the present system are included in Table III.

It is seen from Table III that for D_2 the enthalpy transfer term is endothermic; however, $\delta\Delta H_{tr}{}^{D_2}$ passes through a maximum value of 2.7 kcal/mol at ~35 mol % Me_2SO and then gradually decreases to 2.1 kcal/mol. Hydroxide ion experiences an initial slight exothermic process, with $\delta\Delta H_{tr}{}^{OH^-} = -0.8$ kcal/mol at 10 mol % Me_2SO, but thereafter the process becomes strongly endothermic, with $\delta\Delta H_{tr}{}^{OH^-}$ reaching 17.5 kcal/mol in 96.9 mol % Me_2SO. The sum of the constituent terms for the reactants in the isotopic exchange process, $\delta\Delta H_{tr}{}^{R} = \delta\Delta H_{tr}{}^{D_2} + \delta\Delta H_{tr}{}^{OH^-}$, is shown graphically in Figure 2 for the whole solvent composition range. $\delta\Delta H_{tr}{}^{R}$ increases only slightly until 10% Me_2SO, more strongly till 40% Me_2SO, then levels off somewhat. At 96.9 mol % Me_2SO, $\delta\Delta H_{tr}{}^{R} = 19.6$ kcal/mol.

The transition state enthalpy of transfer, $\delta\Delta H_{tr}{}^{t}$, from water to an aqueous Me_2SO medium may be calculated[12-15] from $\delta\Delta H_{tr}{}^{t} = \delta\Delta H_{tr}{}^{R} + \delta\Delta H^\ddagger$. Here $\delta\Delta H^\ddagger$ is the difference in the enthalpies of activation between the two media, i.e., $\delta\Delta H^\ddagger = \Delta H^\ddagger(x\%\ Me_2SO) - \Delta H^\ddagger(H_2O)$, and $\delta\Delta H_{tr}{}^{R}$ is as defined previously. Values of $\delta\Delta H_{tr}{}^{t}$ thus calculated for the entire region of medium composition are given in Table III and shown in Figure 2.

From Figure 2 it is apparent that the transition-state enthalpy transfer from water to aqueous Me_2SO is endothermic and that the endothermicity increases markedly as the

Table III. Enthalpies of Transfer (kcal/mol) for Reactants and for the Transition State of the D_2–OH^- Exchange Process in the Me_2SO–H_2O System[a]

Me_2SO, mol %	$\delta\Delta H_{tr}{}^{D_2}$	$\delta\Delta H_{tr}{}^{OH^-}$	$\delta\Delta H_{tr}{}^{R}$	$\Delta H^\ddagger$	$\delta\Delta H^\ddagger$	$\delta\Delta H_{tr}{}^{t}$
0	0	0	0	24.0	0	0
10	1.2	−0.8	0.4			
20.2	2.1	+3.7	5.8	21.2	−2.8	3.0
40.1	2.6	10.1	12.7	17.7	−6.3	6.4
59.0	2.2	13.8	16.0	16.4	−7.6	8.4
77.9	2.1	16.0	18.1	16.9	−7.1	11.0
87.5	2.1	16.9	19,0	16.8	−7.2	11.8
96.9	2.1	17.5	19.6	18.1	−5.9	13.7

[a] $\delta\Delta H_{tr}{}^{D_2}$ from ref 18; $\delta\Delta H_{tr}{}^{OH^-}$ from ref 16; $\Delta H^\ddagger$ values determined in this work (see Table II) except value for 0% Me_2SO which is taken from ref 4. $\delta\Delta H_{tr}{}^{t}$ calculated from $\delta\Delta H_{tr}{}^{t} = \delta\Delta H_{tr}{}^{R} + \delta\Delta H^\ddagger$.

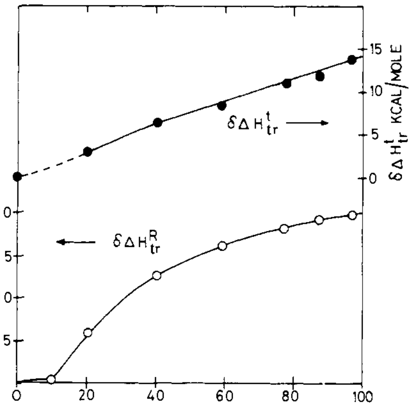
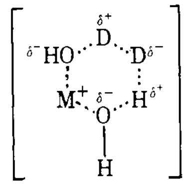


Figure 2. Enthalpies of transfer for reactants ($\delta\Delta H_{tr}{}^{R}$) and for the transition state ($\delta\Delta H_{tr}{}^{t}$) of the D_2-OH^- exchange process in H_2O-Me_2SO mixtures.

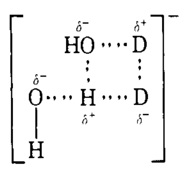
Me_2SO content is increased. This is contrary to the situation found in reactions such as nucleophilic displacement at saturated carbon or at aromatic carbon, where the corresponding transition-state enthalpy transfer term is generally strongly exothermic.[12,13] However, the present reaction shows some similarity to alkaline ester hydrolysis,[14,15] in which case the transition-state enthalpy transfer is also endothermic, though not nearly to the same degree as in the present system.

The degree of endothermicity for the transition-state transfer in the present system is quite remarkable, with $\delta\Delta H_{tr}{}^{t}$ reaching a maximum value of 13.7 kcal/mol in 96.9 mol % Me_2SO. This desolvation energy is about two-thirds of $\delta\Delta H_{tr}{}^{R}$, the desolvation energy of reactants from aqueous medium to 96.9 mol % Me_2SO. Evidently the destabilization of OH^- (noting that $\delta\Delta H_{tr}{}^{OH^-}$ is the major component of $\delta\Delta H_{tr}{}^{R}$ in Me_2SO rich media) is largely retained in the transition state. It is also interesting that, in >40 mol % Me_2SO, $\delta\Delta H_{tr}{}^{t}$ increases almost linearly whereas the $\delta\Delta H_{tr}{}^{R}$ function shows slight downward curvature. Therefore, if the enthalpy terms were the only ones controlling the rate of reaction, a decreased rate would result on increasing the Me_2SO content above ~60 mol %. However, the increasing $\Delta S^\ddagger$ term over this region (Figure 1) compensates for the divergence between the $\delta\Delta H_{tr}{}^{t}$ and $\delta\Delta H_{tr}{}^{R}$ terms, resulting in a net increase in reaction rate.

Mechanistic Implications. The substantial desolvation of the transition state on transfer from water to aqueous Me_2SO media must be of primary concern in consideration of mechanisms for isotopic exchange. It appears that only those mechanisms which retain a substantial degree of charge localization on electronegative atoms in the rate-determining transition state may be retained for serious consideration. Therefore, we may exclude certain cyclic transition states such as A[1] and B:[26]



A



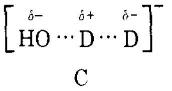
B

Structure A had been proposed[1] to take into account the possibility of mechanisms requiring ion pairing between the cation (M^+) and hydroxide ion, as well as electrophilic assistance from a solvent molecule which may be coordinated to M^+. In the four-centered cyclic transition state B, the H_2O molecule providing electrophilic assistance is considered to be one of the molecules solvating the attacking hydroxide ion; OH^- is usually assigned three H_2O molecules in its first solvation sphere.[27] In both A and B there will be an internal charge dispersal since, in the cyclic transition states, the various bond-making and bond-breaking processes occur concertedly. Additionally, in A, the negative charge on OH^- is effectively neutralized by the coordinated counterion M^+. Therefore, if the exchange mechanism involved the rate-determining transition states A or B, only moderate desolvation should accompany changing the medium from aqueous to Me_2SO rich; this should be reflected in small $\delta\Delta H_{tr}{}^{t}$ values, contrary to observations.

For isotopic exchange involving proton transfer between base and a weak acid (D_2), the simplest mechanism is probably the two-stage process, eq 2 and 3. The first stage (eq 2) involves rate-determining abstraction of a proton from D_2 leaving temporarily a deuteride ion. In the second stage (eq 3) D^- is rapidly discharged by reaction with the proton donor, H_2O, yielding DH and regenerating OH^-. The transition state of the rate-determining step is C.

$$HO^- + D\text{—}D \xrightarrow{\text{slow}} HOD + D^- \qquad (2)$$

$$D^- + HOH \xrightarrow{\text{fast}} DH + OH^- \qquad (3)$$

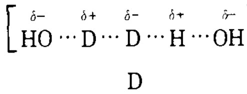


$$\left[\overset{\delta-}{HO}\cdots\overset{\delta+}{D}\cdots\overset{\delta-}{D}\right]^-$$

C

Formation of free deuteride ion can be circumvented by direct participation of a water molecule in the rate-determining step in order to provide electrophilic assistance for removal of D^- (eq 4) and thereby avoid formation of a high-energy intermediate.[28] The transition state D would have the probable charge distribution indicated.

$$HO^- + D\text{—}D + HOH \longrightarrow HOD + DH + OH^- \qquad (4)$$



$$\left[\overset{\delta-}{HO}\cdots\overset{\delta+}{D}\cdots\overset{\delta-}{D}\cdots\overset{\delta+}{H}\cdots\overset{\delta-}{OH}\right]^-$$

D

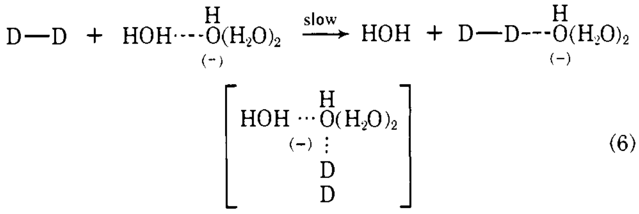
It is rather difficult to make an enlightened choice between the mechanisms given by eq 2, 3, and 4. In the latter case the negative charge in the transition state D, though less localized than in the reacting OH^-, is nevertheless largely retained on electronegative oxygen atoms. Formation of the transition state will therefore be accompanied by somewhat smaller solvation requirements compared with the reactants, leading to $\delta\Delta H_{tr}^{\ddagger}$ being moderately smaller than $\delta\Delta H_{tr}^{R}$, as observed.

For the mechanism of eq 2 and 3, the rate-determining transition state has the negative charge residing in part on oxygen and in part on deuterium. Now deuteride (hydride) ion is considered to be a "soft", polarizable base on the scale which puts negatively charged oxygen a "hard", nonpolarizable base.[29] To the extent that charge is generated on the deuterium, the solvation requirements will be reduced in the transition state C relative to the reactants, and also relative to transition state D. The lesser solvation of C than of D would lead to a smaller $\delta\Delta H_{tr}^{\ddagger}$ for the former case. Since the data of Table III point to large solvation requirements of the transition state, the mechanism of eq 4 appears to be the more favored one. It is interesting to note that as the % Me_2SO is increased, the concomitant desolvation of the reacting hydroxide ion will cause it to become more basic.[30,31] This in turn will lead to more reactant-like transition states,[32] with a greater negative charge concentrated on the attacking oxygen.

A novel approach to the D_2 exchange problem was put forth by Ritchie and King[33] as a result of ab initio (LCAO-MO-SCF) calculations. These indicated that the *gas-phase* reaction of HO^- with H_2 yielding H_2O and H^-, or the reverse process, proceeds by way of a metastable addition complex $[HOHH]^-$, the formation of which is *not* associated with a classical activation energy. It was concluded therefore that the activation energy associated with isotopic exchange *in solution* (ca. 24 kcal/mol) arises from the required partial desolvation of hydroxide ion before that can react with D_2 to yield the adduct $[HODD]^-$; a fast step with H_2O then yields the products of exchange:

$$HO{-}D{-}D^- + HOH \xrightarrow{\text{fast}} HOD + DH + OH^- \quad (5)$$

This proposal can accommodate our present results when it is borne in mind that, in aqueous medium, hydroxide ion is considered to be solvated by three molecules of H_2O.[27] Thus the rate-determining step for isotopic exchange becomes the replacement of one molecule of H_2O in the primary solvation shell of OH^- by D_2.[34] This can be represented by eq 6 for which the transition state is given by E:



$$D{-}D + HOH\cdots\underset{(-)}{\overset{H}{O}}(H_2O)_2 \xrightarrow{\text{slow}} HOH + D{-}D{-}{-}{-}\underset{(-)}{\overset{H}{O}}(H_2O)_2$$

$$\left[\begin{array}{c} HOH\cdots\overset{H}{O}(H_2O)_2 \\ (-)\ \vdots \\ D \\ D \end{array}\right] \quad (6)$$

E

The product in eq 6 has the essential character of the addition complex put forth by Ritchie and King, but solvated by two molecules of H_2O.

It is apparent that the transition state of this process, E, has a considerable solvation requirement so that one would expect an appreciable medium effect on transfer from water to Me_2SO, i.e., a substantial $\delta\Delta H_{tr}^{\ddagger}$ value. If the reasonable assumption is made that E resembles the intermediate complex structurally, i.e., that bond formation to DD and bond rupture from HOH is well advanced, then solvation of the transition state will be about two-thirds of that of the reactants, hydroxide ion and D_2, bearing in mind that the hydroxide ion term predominates. On this basis the $\delta\Delta H_{tr}^{\ddagger}$ term should be about two-thirds as large as $\delta\Delta H_{tr}^{R}$ but should decrease somewhat in media of low Me_2SO content in which the $\delta\Delta H_{tr}^{D_2}$ term contributes more appreciably. In practice (see Table III), $\delta\Delta H_{tr}^{\ddagger}/\delta\Delta H_{tr}^{R}$ decreases from 0.7 in the high Me_2SO composition range to 0.5 in media of low Me_2SO content, which is in agreement with the above considerations and tends to support the addition complex mechanism for D_2-OH^- exchange. However, decision as to the actual operating mechanism (eq 2–6) is perhaps best deferred until further mechanistic criteria become available, for example, measurements of kinetic isotope effects.

The Me_2SO-water solvent system is recognized to be structured.[35,36] A variety of physical properties indicate that maximum structure corresponds to a 2:1 M composition of H_2O and Me_2SO (e.g., viscosities, refractive indexes, enthalpies of solution, etc. often exhibit extrema at this composition). It might have been expected, therefore, that in D_2 exchange some characteristic property of reaction would also exhibit an extremum at that solvent composition. It is interesting then that though $\delta\Delta H_{tr}^{H_2}$ exhibits a relatively low maximum at 33 mol % Me_2SO, $\delta\Delta H_{tr}^{OH^-}$ does not, and neither does $\delta\Delta H_{tr}^{R}$. It is also significant that $\delta\Delta H_{tr}^{\ddagger}$ is a smooth function of the Me_2SO composition.

An extremum is found, however, in one of the experimental properties recorded in this work, namely in the $\Delta S^{\ddagger}$ function in the region of 60 mol % Me_2SO. Since entropies of activation are believed to reflect the organization of solvent molecules in the transition state relative to the reactants,[37] it would clearly be desirable to be able to dissect the terms $\delta\Delta S_{tr}^{R}$, $\delta\Delta S_{tr}^{\ddagger}$, and $\delta\Delta S^{\ddagger}$ corresponding to the dissection of the $\delta\Delta H_{tr}$ terms in this work. Unfortunately presently available data for $\delta\Delta S_{tr}^{OH^-}$ cover only part of the Me_2SO-water system.[38] The important role of entropies of activation in this reaction is clearly shown by the fact that, in >60 mol % Me_2SO, where $\delta\Delta H_{tr}^{\ddagger}$ diverges from $\delta\Delta H_{tr}^{R}$, the increase in reaction rate is brought about by the contribution of the $\Delta S^{\ddagger}$ term.

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Normal Coordinates, Structure, and Bonding of Benzyne

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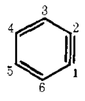
Abstract: On the basis of the observed matrix-infrared spectrum of benzyne, a structure and set of force constants and bond orders are proposed, other possible structures are ruled out, and predictions are made of yet-unobserved frequencies and of the vibrational spectrum of benzyne-d_4.

Benzyne, or 1,2-dehydrobenzene, has offered a challenge to our capacities to infer structures and bonding, ever since its existence was demonstrated.[1,2] The reactivity of benzyne—the apparently very low or zero activation energy of dimerization, for example—indicates that the species is more like a diradical than a benzene with an extra electron-pair bond.[3,4] Yet there is no indication that the ground state of benzyne is anything but a closed-shell singlet.[1,5] The qualitative picture in vogue supposes that benzyne's "triple" bond is shorter than the 1.39 Å of a normal benzenoid bond because two electrons occupy a *weakly* bonding orbital whose maximum electron density lies in the molecular plane, and whose parentage in benzyne can be traced to the C-atom orbital contributions from the vicinal C–H bonds of benzene that no longer exist in benzyne. If this is so, then presumably there is some strain-induced rehybridization, making the atomic carbon orbitals of the "triple" bond more than one-third p-like, and (see Figure 1) giving the orbitals of the adjacent C–C bonds a hybridization between sp^2 and sp. The bond lengths and bond orders of benzyne were first estimated previously in connection with semiempirical theoretical calculations.[6] Some calculations indicate a shortening of the C_1–C_2 bond and lengthening of the C_4–C_5 bond, and a "triple bond" structure, although one calculation suggests a cumulene-like structure.[7]

The only experimental hints directly cogent to the geometry and bonding of benzyne come from the infrared spectrum of the species frozen in an inert matrix. This spectrum was obtained by Chapman, Mattes, McIntosh, Pacansky, Calder, and Orr.[8] The microwave spectrum has not been reported and the electronic spectrum[9] appears to consist of a featureless continuum whose energy range and intensity are consistent with the interpretation just given for the "triple" bond, that the "in-plane" carbon orbitals form ethylene-like bonding and antibonding orbitals whose bonding and antibonding strength are both significantly weaker than in a normal 2pπ olefinic bond. However, the electronic spectrum contributes no positive information about the structure.

We report here an interpretation of the infrared vibrational spectrum of benzyne, as reported by Chapman et al.,[8] from which we infer the normal coordinates, the bond lengths, and bond orders and predict the infrared spectrum of benzyne-d_4. We shall show that its infrared spectrum implies that benzyne has alternating bond lengths consistent with the aryne-like structure I.



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Analysis of Data

The infrared spectrum of benzyne between 400 and 1700 cm^{-1} was reported by Chapman et al. to exhibit eight bands, at 469, 736, 849, 1038, 1053, 1451, 1607, and 1627 cm^{-1}. No spectrum was reported for higher frequencies. We assume that the benzyne molecule has C_{2v} symmetry. The molecule has normal modes of vibration that transform according to the four symmetry species of this point group, as follows: A_1, nine; A_2, four; B_1, three, and B_2, eight. The A_2 and B_1 species represent out-of-plane motion and the A_1 and B_2 species, in-plane motion. The A_2 modes are infrared-inactive but Raman-active; the other three sets of modes are infrared-active.

We carried out a normal mode analysis with a valence force field model, in which we allowed some variation of the bond lengths and angles, as well as of force constants, to optimize the fit between model and observation. Specifically, we assume that

$$t_1 = R(C_3\text{-}C_4) = R(C_5\text{-}C_6)$$

$$t_4 = R(C_1\text{-}C_6) = R(C_2\text{-}C_3)$$

and define

$$t_2 = R(C_4\text{-}C_5)$$

$$t_5 = R(C_1\text{-}C_2)$$